

PATENT

ATTORNEY DOCKET NO.: KCX-50

(13,101) (12,865)

(12,739) (12,731)

UNITED STATES PATENT APPLICATION

OF

MARK M. MLEZIVA

KURTIS L. BROWN

CHRISTOPHER C. CREAGAN

SAMUEL E. MARMON

AND

DARRYL F. CLARK

FOR

CRIMPED MULTICOMPONENT FILAMENTS AND SPUNBOND WEBS

MADE THEREFROM

PATENT

ATTORNEY DOCKET NO.: KCX-50

(13,101) (12,865)

(12,739) (12,731)

**CRIMPED MULTICOMPONENT FILAMENTS
AND SPUNBOND WEBS MADE THEREFROM**

Field of the Invention

The present invention is generally directed to spunbond multicomponent filaments and to nonwoven webs made from the filaments. More particularly, the present invention is directed to incorporating an additive into one of the polymers used to make multicomponent filaments. The additive enhances crimp, allows for finer filaments, improves the integrity of unbonded webs made from the filaments, enhances bonding of the filaments, and produces webs with improved stretch and cloth-like properties. The additive incorporated into the filaments is a butylene-propylene random copolymer.

Background of the Invention

Nonwoven fabrics are used to make a variety of products which desirably have particular levels of softness, strength, uniformity, liquid handling properties such as absorbency, and other physical properties. Such products include towels, industrial wipers, incontinence products, filter products, infant care products such as baby diapers, absorbent feminine care products, and garments such as medical apparel. These products are often made with multiple layers of nonwoven fabrics to obtain the desired combination of properties. For example, disposable baby diapers made from polymeric nonwoven fabrics may include a soft and porous liner layer which fits next to the baby's skin, an impervious outer cover layer which is strong and soft, and one or more interior liquid

handling layers which are soft, bulky and absorbent.

Nonwoven fabrics such as the foregoing are commonly made by melt spinning thermoplastic materials. Such fabrics are called spunbond materials. Spunbond nonwoven polymeric webs are typically made from thermoplastic materials by extruding the thermoplastic material through a spinneret and drawing the extruded material into filaments with a stream of high velocity air to form a random web on a collecting surface.

Spunbond materials with desirable combinations of physical properties, especially combinations of softness, strength and absorbency, have been produced, but limitations have been encountered. For example, for some applications, polymeric materials such as polypropylene may have a desirable level of strength but not a desirable level of softness. On the other hand, materials such as polyethylene may, in some cases, have a desirable level of softness but not a desirable level of strength.

In an effort to produce nonwoven materials having desirable combinations of physical properties, nonwoven polymeric fabrics made from multicomponent or bicomponent filaments and fibers have been developed. Bicomponent or multicomponent polymeric fibers or filaments include two or more polymeric components which remain distinct. As used herein, filaments mean continuous strands of material and fibers mean cut or discontinuous strands having a definite length. The first and subsequent components of multicomponent filaments are arranged in substantially distinct zones across the cross-section of the filaments and extend continuously along the length of the filaments. Typically, one component exhibits different properties than the other so that the filaments exhibit properties of the two components. For

example, one component may be polypropylene which is relatively strong and the other component may be polyethylene which is relatively soft. The end result is a strong yet soft nonwoven fabric.

To increase the bulk or fullness of the bicomponent nonwoven webs for improved fluid management performance or for enhanced "cloth-like" feel of the webs, the bicomponent filaments or fibers are often crimped. Bicomponent filaments may be either mechanically crimped or, if the appropriate polymers are used, naturally crimped. As used herein, a naturally crimped filament is a filament that is crimped by activating a latent crimp contained in the filaments. For instance, in one embodiment, filaments can be naturally crimped by subjecting the filaments to a gas, such as a heated gas, after being drawn.

In general, it is far more preferable to construct filaments that can be naturally crimped as opposed to having to crimp the filaments in a separate mechanical process. Difficulties have been experienced in the past, however, in producing filaments that will crimp naturally to the extent required for the particular application. Also, it has been found to be very difficult to produce naturally crimped fine filaments, such as filaments having a linear density of less than 2 denier. Specifically, the draw force used to produce fine filaments usually prevents or removes any meaningful latent crimp that may be contained in the filaments. As such, currently a need exists for a method of producing multicomponent filaments with enhanced natural crimp properties. Also, a need exists for nonwoven webs made from such filaments.

Summary of the Invention

The present invention recognizes and addresses the foregoing disadvantages, and others of prior art constructions and methods.

Accordingly, an object of the present invention is to provide improved nonwoven fabrics and methods for making the same.

Another object of the present invention is to provide nonwoven polymeric fabrics including highly crimped filaments and methods for economically making the same.

A further object of the present invention is to provide a method for controlling the properties of a nonwoven polymeric fabric by varying the degree of crimp of filaments and fibers used to make the fabric.

Another object of the present invention is to provide an improved process for naturally crimping multicomponent filaments.

It is another object of the present invention to provide a method for naturally crimping multicomponent filaments by adding to one of the components of the filaments a butylene-propylene copolymer.

Still another object of the present invention is to provide a naturally crimped filament that has a linear density of less than 2 denier.

Another object of the present invention is to provide a bicomponent filament made from polypropylene and polyethylene, wherein a crimp enhancement additive has been added to the polyethylene.

It is still another object of the present invention to provide a process for naturally crimping multicomponent filaments containing polypropylene and polyethylene in which a crimp

enhancement additive and reclaimed polymer has been added to the polyethylene.

Another object of the present invention is to provide a crimp enhancement additive that also improves the strength of unbonded webs made from filaments containing the additive.

These and other objects of the present invention are achieved by providing a process for forming a nonwoven web. The process includes the steps of melt spinning multicomponent filaments. The multicomponent filaments include a first polymeric component and a second polymeric component. The first polymeric component has a faster solidification rate than the second polymeric component for providing the filaments with a latent crimp. The second polymeric component contains a crimp enhancement additive that is a butylene-propylene copolymer.

Once melt spun, the multicomponent filaments are drawn and naturally crimped. Thereafter, the multicomponent crimped filaments are formed into a nonwoven web for use in various applications.

In one embodiment, the second polymeric component can include polyethylene. The butylene-propylene copolymer can be added to the second polymeric component in an amount less than about 10% by weight, and particularly from about 0.5% to about 5% by weight. Preferably, the butylene-propylene copolymer is a random copolymer containing less than about 20% by weight butylene, and particularly about 14% by weight butylene.

The first polymeric component, on the other hand, in one preferred embodiment is polypropylene.

Other polymers that may be used include nylon, polyester and copolymers of polypropylene, such as a propylene-ethylene copolymer.

In accordance with the present invention, it has been also discovered that the butylene-propylene copolymer also functions as a polymer compatibilizer. In particular, it has been found that the copolymer allows better homogeneous mixing between different polymers. In this regard, the first polymeric component, in accordance with the present invention, can also contain reclaim polymer. Reclaim polymer, as used herein, are polymer scraps that are recycled and added to the filaments. For instance, the reclaim polymer can comprise a mixture of polyethylene, polypropylene, and copolymers of propylene and ethylene, and can be obtained from the trimmed edges of previously formed nonwoven webs. In the past, difficulties were experienced in recycling reclaim polymer, especially bicomponent reclaim polymer, and incorporating them into filaments without adversely affecting the physical properties of the filaments.

These and other objects of the present invention are also achieved by providing a nonwoven web made from spunbond multicomponent, crimped filaments. The multicomponent crimped filaments are made from at least a first polymeric component and a second polymeric component. In particular, the polymeric components are selected such that the first polymeric component has a faster solidification rate than the second polymeric component. In accordance with the present invention, the second polymeric component contains a crimp enhancement additive. Specifically, the crimp enhancement additive is a butylene-propylene random copolymer.

For instance, in one embodiment, the crimped filaments can be bicomponent filaments which include a polypropylene component and a polyethylene component. The butylene-propylene

random copolymer can be added to the polyethylene component in an amount up to about 5% by weight. Preferably, the butylene-propylene random copolymer contains about 14% by weight butylene.

Because of the addition of the crimp enhancement additive, the multicomponent filaments can have a very low denier and still be crimped naturally. For instance, the denier of the filaments can be less than 2, and particularly less than about 1.2.

In this regard, the present invention is also directed to a naturally crimped multicomponent filament that includes at least a first polymeric component and a second polymeric component. The first polymeric component can be, for instance, polypropylene. The second polymeric component, on the other hand, can be, for instance, polyethylene and can contain a crimp enhancement additive in an amount sufficient to allow the filaments to be naturally crimped at a denier of less than about 2 and particularly less than about 1.2.

Other objects, features and aspects of the present invention are discussed in greater detail below.

Brief Description of the Drawings

A full and enabling disclosure of the present invention, including the best mode thereof, to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figures, in which:

FIG. 1 is a schematic drawing of a process line for making a preferred embodiment of the present invention;

FIG. 2A is a schematic drawing illustrating the cross section of a filament made according to an embodiment of the present invention with the

polymer components **A** and **B** in a side-by-side arrangement; and

FIG. 2B is a schematic drawing illustrating the cross section of a filament made according to an embodiment of the present invention with the polymer components **A** and **B** in a eccentric sheath/core arrangement.

Repeat use of reference characters in the present specification and drawings is intended to represent same or analogous features or elements of the invention.

Detailed Description of Preferred Embodiments

It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary construction.

The present invention is generally directed to multicomponent filaments and to spunbond webs produced from the filaments. In particular, the filaments are naturally crimped into, for instance, a helical arrangement. Crimping the filaments increases the bulk, the softness, and the drapability. The nonwoven webs also have improved fluid management properties and have an enhanced cloth-like appearance and feel.

Multicomponent filaments for use in the present invention contain at least two polymeric components. The polymeric components can be, for instance, in a side-by-side configuration or in an eccentric sheath-core configuration. The polymeric components are selected from semi-crystalline and crystalline thermoplastic polymers which have different solidification rates with respect to each other in order for the filaments to undergo natural

crimping. More particularly, one of the polymeric components has a faster solidifying rate than the other polymeric component.

As used herein, the solidification rate of a polymer refers to the rate at which a softened or melted polymer hardens and forms a fixed structure.

It is believed that the solidification rate of a polymer is influenced by different parameters including the melting temperature and the rate of crystallization of the polymer. For instance, a fast solidifying polymer typically has a melting point that is about 10° C or higher, more desirably about 20° C or higher, and most desirably about 30° C or higher than a polymer that has a slower solidifying rate. It should be understood, however, that both polymeric components may have similar melting points if their crystallization rates are measurably different.

Although unknown, it is believed that the latent crimpability of multicomponent filaments is created in the filaments due to the differences in the shrinkage properties between the polymeric components. Further, it is believed that the main cause of the shrinkage difference between polymeric components is the incomplete crystallization of the slower solidifying polymer during the fiber production process. For instance, during formation of the filaments, when the fast solidifying polymer is solidified, the slow solidifying polymer is partially solidified and does not measurably draw any longer and thus does not further experience a significant orienting force. In the absence of an orienting force, the slow solidified polymer does not significantly further crystallize while being cooled and solidified. Accordingly, the resulting filaments possess latent crimpability, and such latent crimpability can be activated by subjecting

the filaments to a process that allows sufficient molecular movement of the polymer molecules of the slow solidifying polymer to facilitate further crystallization and shrinkage.

The present invention is directed to adding a crimp enhancement additive to the polymeric component having the slower solidification rate in order to further slow the solidification rate of the polymer. In this manner, the differences between the solidification rates of both polymeric components becomes even greater creating multicomponent filaments that have an enhanced latent crimpability. In particular, the crimp enhancement additive of the present invention is a random butylene-propylene copolymer.

Besides creating multicomponent filaments that have a greater natural crimp, it has also been discovered that the crimp enhancement additive of the present invention provides many other benefits and advantages. For instance, because the filaments of the present invention have a greater degree of crimping, fabrics and webs made from the filaments have a higher bulk and a lower density. By being able to make lower density webs, less material is needed to make webs of a specified thickness and the webs are thus less expensive to produce. Besides having lower densities, the webs have also been found to be more cloth-like, to have a softer hand, to have more stretch, to have better recovery, and to have better abrasion resistance.

Of particular advantage, it has also been unexpectedly discovered that the crimp enhancement additive of the present invention further improves the strength and integrity of unbonded webs made from the filaments. For instance, it was discovered that adding only 1% by weight of the additive can more than double the unbonded strength

of the web. By having greater unbonded web integrity, the webs of the present invention may be processed at faster speeds. In the past, in order to run at higher speeds, unbonded spunbond webs had to be prebonded or compacted. Such steps are not necessary when processing webs made according to the present invention.

Besides have increased strength, spunbond webs made according to the present invention also have dramatically reduced web handling problems when processed at higher speeds. For instance, the occurrences of eyebrows, flip overs and stretch marks are significantly reduced when the crimp enhancement additive is present within the filaments. More particularly, webs incorporating filaments made according to the present invention have a lesser tendency to protrude from the web but, instead, have a greater tendency to lay down on the web surface. As such, the filaments are less likely to penetrate the foraminous surface upon which the web is formed, thus making it easier to remove the web from the surface.

Another unexpected benefit to using the crimp enhancement additive of the present invention is that the additive also functions as polymer compatibilizer. In other words, the additive facilitates homogeneous mixing of different polymers. Thus, the polymeric component containing the additive can contain a mixture of polymers if desired. For example, in one embodiment of the present invention, the polymeric component containing the additive of the present invention can also contain reclaim polymer, such as polymeric scraps collected from the trimmings of previously formed spunbond webs and particularly bicomponent webs.

A further advantage to the crimp enhancement additive of the present invention is that the additive permits the formation of very fine multicomponent filaments having a relatively high natural crimp. In the past, it was very difficult to create fine filaments, such as at less than 2 denier, that had a relatively high natural crimp. In the past, the draw force used to produce fine fibers usually prevented or removed any meaningful latent crimp present within the filaments. Filaments made according to the present invention, on the other hand, can have greater than 10 crimps per inch at less than 2 denier, and even lower than 1.2 denier.

Besides the above-listed advantages, it has also been discovered that the crimp enhancement additive of the present invention improves thermal bonding between the filaments. In particular, the crimp enhancement additive has a broad melting point range and has a relatively low melt temperature, which facilitates bonding.

The webs and fabrics of the present invention are particularly useful for making various products including liquid and gas filters, personal care articles and garment materials. Personal care articles include infant care products such as disposable baby diapers, child care products such as training pants, and adult care products such as incontinence products and feminine care products. Suitable garments include medical apparel, work wear, and the like.

As described above, the fabric of the present invention includes continuous multicomponent polymeric filaments comprising at least first and second polymeric components. A preferred embodiment of the present invention is a polymeric fabric including continuous bicomponent filaments

comprising a first polymeric component **A** and a second polymeric component **B**. The bicomponent filaments have a cross-section, a length, and a peripheral surface. The first and second components **A** and **B** are arranged in substantially distinct zones across the cross-section of the bicomponent filaments and extend continuously along the length of the bicomponents filaments. The second component **B** constitutes at least a portion of the peripheral surface of the bicomponent filaments continuously along the length of the bicomponent filaments.

The first and second components **A** and **B** are arranged in either a side-by-side arrangement as shown in **FIG. 2A** or an eccentric sheath/core arrangement as shown in **FIG. 2B** so that the resulting filaments exhibit a natural helical crimp. Polymer component **A** is the core of the filament and polymer component **B** is the sheath in the sheath/core arrangement. Methods for extruding multicomponent polymeric filaments into such arrangements are well-known to those of ordinary skill in the art.

A wide variety of polymers are suitable to practice the present invention including polyolefins (such as polyethylene and polypropylene), polyesters, polyamides, and the like. Polymer component **A** and polymer component **B** must be selected so that the resulting bicomponent filament is capable of developing a natural helical crimp. Preferably, polymer component **A** has a faster solidification rate than polymer component **B**. For instance, in one embodiment, polymer component **A** can have a higher melting temperature than polymer component **B**.

Preferably, polymer component **A** comprises polypropylene or a random copolymer of propylene and ethylene. Besides containing polypropylene, polymer component **A** can also be a nylon or a polyester.

Polymer component **B**, on the other hand, preferably comprises polyethylene or a random copolymer of propylene and ethylene. Preferred polyethylenes include linear low density polyethylene and high density polyethylene.

Suitable materials for preparing the multicomponent filaments of the present invention include PD-3445 polypropylene available from Exxon of Houston, Tex., random copolymer of propylene and ethylene available from Exxon, ASPUN 6811A and 2553 linear low density polyethylene available from the Dow Chemical Company of Midland, Mich., 25355 and 12350 high density polyethylene available from the Dow Chemical Company.

When polypropylene is component **A** and polyethylene is component **B**, the bicomponent filaments may comprise from about 20 to about 80% by weight polypropylene and from about 20 to about 80% polyethylene. More preferably, the filaments comprise from about 40 to about 60% by weight polypropylene and from about 40 to about 60% by weight polyethylene.

As described above, the crimp enhancement additive of the present invention is a random copolymer of butylene and propylene and is added to polymer component **B** which is preferably polyethylene. The butylene-propylene random copolymer preferably contains from about 5% to about 20% by weight butylene. For instance, one commercially available product that may be used as the crimp enhancement additive is Product No.

DS4D05 marketed by the Union Carbide Corporation of Danbury, Connecticut. Product No. DS4D05 is a butylene-propylene random copolymer containing 14% by weight butylene and 86% by weight propylene. Preferably, the butylene-propylene copolymer is a film grade polymer having an MFR (melt flow rate) of from about 3.0 to about 15.0, and particularly having a MFR of from about 5 to about 6.5.

In order to combine the crimp enhancement additive with polymer component **B**, in one embodiment, the polymers can be dry blended and extruded together during formation of the multicomponent filaments. In an alternative embodiment, the crimp enhancement additive and polymer component **B** which can be, for instance, polyethylene, can be melt blended prior to being formed into the filaments of the present invention.

In general, the crimp enhancement additive can be added to polymeric component **B** in an amount less than 10% by weight. When polymeric component **B** contains polyethylene, preferably the crimp enhancement additive is added in an amount from about 0.5% to about 5% by weight based upon the total weight of polymer component **B**. Should too much of the butylene-propylene random copolymer be added to the polymer component, the resulting filaments may become too curly and adversely interfere with the formation of a nonwoven web.

It is believed that the butylene-propylene random copolymer, when added to a polymer such as polyethylene, slows the solidification rate and the crystallization rate of the polymer. In this manner, a greater difference in solidification rates is created between the different polymer components used to make the filaments, thereby

increasing the latent crimpability of the filaments.

In an alternative embodiment of the present invention, besides adding the crimp enhancement additive to polymer component **B**, reclaimed and recycled polymers are also added to the polymer component. As described above, it has been discovered that the crimp enhancement additive of the present invention also facilitates homogeneous mixing between polymers. Specifically, the butylene-propylene random copolymer has been found to facilitate mixing between polyethylene and a reclaim polymer that contains a mixture of polyethylene and polypropylene. In this embodiment, the reclaim polymer can be added to the polymeric component in an amount up to about 20% by weight. Preferably, the reclaim polymer is collected from scraps and trimmings of previously formed nonwoven webs. Being able to recycle such polymers not only decreases the amount of materials needed to make the nonwoven webs of the present invention, but also limits the amount of waste that is produced.

One process for producing multicomponent filaments and nonwoven webs according to the present invention will now be discussed in detail with reference to Figure 1. The following process is similar to the process described in U.S. Patent No. 5,382,400 to Pike et al., which is incorporated herein by reference in its entirety.

Turning to **FIG. 1**, a process line **10** for preparing a preferred embodiment of the present invention is disclosed. The process line **10** is arranged to produce bicomponent continuous filaments, but it should be understood that the present invention comprehends nonwoven fabrics made with multicomponent filaments having more than two

components. For example, the fabric of the present invention can be made with filaments having three or four components.

The process line 10 includes a pair of extruders 12a and 12b for separately extruding a polymer component A and a polymer component B. Polymer component A is fed into the respective extruder 12a from a first hopper 14a and polymer component B is fed into the respective extruder 12b from a second hopper 14b. Polymer components A and B are fed from the extruders 12a and 12b through respective polymer conduits 16a and 16b to a spinneret 18.

Spinnerets for extruding bicomponent filaments are well-known to those of ordinary skill in the art and thus are not described here in detail. Generally described, the spinneret 18 includes a housing containing a spin pack which includes a plurality of plates stacked one on top of the other with a pattern of openings arranged to create flow paths for directing polymer components A and B separately through the spinneret. The spinneret 18 has openings arranged in one or more rows. The spinneret openings form a downwardly extending curtain of filaments when the polymers are extruded through the spinneret. For the purposes of the present invention, spinneret 18 may be arranged to form side-by-side or eccentric sheath/core bicomponent filaments illustrated in FIGS. 2A and 2B.

The process line 10 also includes a quench blower 20 positioned adjacent the curtain of filaments extending from the spinneret 18. Air

from the quench air blower 20 quenches the filaments extending from the spinneret 18. The quench air can be directed from one side of the filament curtain as shown FIG. 1, or both sides of the filament curtain.

A fiber draw unit or aspirator 22 is positioned below the spinneret 18 and receives the quenched filaments. Fiber draw units or aspirators for use in melt spinning polymers are well-known as discussed above. Suitable fiber draw units for use in the process of the present invention include a linear fiber aspirator of the type shown in U.S. Pat. No. 3,802,817 and educative guns of the type shown in U.S. Patent Nos. 3,692,618 and 3,423,266, the disclosures of which are incorporated herein by reference.

Generally described, the fiber draw unit 22 includes an elongate vertical passage through which the filaments are drawn by aspirating air entering from the sides of the passage and flowing downwardly through the passage. A heater or blower 24 supplies aspirating air to the fiber draw unit 22. The aspirating air draws the filaments and ambient air through the fiber draw unit.

An endless foraminous forming surface 26 is positioned below the fiber draw unit 22 and receives the continuous filaments from the outlet opening of the fiber draw unit. The forming surface 26 travels around guide rollers 28. A vacuum 30 positioned below the forming surface 26 where the filaments are deposited draws the filaments against the forming surface.

The process line 10 further includes a bonding apparatus such as thermal point bonding rollers 34

(shown in phantom) or a through-air bonder 36.

Thermal point bonders and through-air bonders are well-known to those skilled in the art and are not disclosed here in detail. Generally described, the through-air bonder 36 includes a perforated roller 38, which receives the web, and a hood 40 surrounding the perforated roller. Lastly, the process line 10 includes a winding roll 42 for taking up the finished fabric.

To operate the process line 10, the hoppers 14a and 14b are filled with the respective polymer components A and B. Polymer components A and B are melted and extruded by the respective extruders 12a and 12b through polymer conduits 16a and 16b and the spinneret 18. Although the temperatures of the molten polymers vary depending on the polymers used, when polypropylene and polyethylene are used as components A and B respectively, the preferred temperatures of the polymers when extruded range from about 370° to about 530° F. and preferably range from 400° to about 450° F.

As the extruded filaments extend below the spinneret 18, a stream of air from the quench blower 20 at least partially quenches the filaments to develop a latent helical crimp in the filaments.

The quench air preferably flows in a direction substantially perpendicular to the length of the filaments at a temperature of about 45° to about 90° F. and a velocity of from about 100 to about 400 feet per minute.

After quenching, the filaments are drawn into the vertical passage of the fiber draw unit 22 by a flow of a gas, such as air, from the heater or blower 24 through the fiber draw unit. The fiber

draw unit is preferably positioned 30 to 60 inches below the bottom of the spinneret 18. The temperature of the air supplied from the heater or blower 24 is sufficient to activate the latent crimp. The temperature required to activate the latent crimp of the filaments ranges from about 60° F. to a maximum temperature near the melting point of the lower melting component which is the second component B.

The actual temperature of the air being supplied by heater or blower 24 generally will depend upon the linear density of the filaments being produced. For instance, it has been discovered that at greater than 2 denier, no heat is required at the fiber draw unit 22 in order to naturally crimp the filaments, which is a further advantage of the present invention. In the past, air being supplied to the fiber draw unit 22 typically had to be heated. Filaments finer than about 2 denier made according to the present invention, however, generally will need to be contacted with heated air in order to induce natural crimping.

The temperature of the air from the heater 24 can be varied to achieve different levels of crimp. Generally, a higher air temperature produces a higher number of crimps. The ability to control the degree of crimp of the filaments is particularly advantageous because it allows one to change the resulting density, pore size distribution and drape of the fabric by simply adjusting the temperature of the air in the fiber draw unit.

The crimped filaments are deposited through the outlet opening of the fiber draw unit 22 onto

the traveling forming surface 26. The vacuum 20 draws the filaments against the forming surface 26 to form an unbonded, nonwoven web of continuous filaments. In the past, the web was then typically lightly compressed by a compression roller and then thermal point bonded by rollers 34 or through-air bonded in the through-air bonder 36. As described above, however, it has been discovered that nonwoven webs made according to the present invention have increased strength and integrity when containing the crimp enhancement additive. As such, very little prebonding by a compression roller or any other type of prebonding station is necessary in process line 10 prior to feeding the webs to a bonding station. Further, due to the increased strength of nonbonded webs made according to the present invention, line speeds can be increased. For instance, line speeds can range from about 150 feet per minute to about 500 feet per minute.

In the through-air bonder 36 as shown in Figure 1, air having a temperature above the melting temperature of component B and below the melting temperature of component A is directed from the hood 40, through the web, and into the perforated roller 38. The hot air melts the lower melting polymer component B and thereby forms bonds between the bicomponent filaments to integrate the web. When polypropylene and polyethylene are used as polymer components A and B respectively, the air flowing through the through-air bonder preferably has a temperature ranging from about 230° to about 280° F. and a velocity from about 100 to about 500 feet per minute. The dwell time of the web in the through-air bonder is preferably less than about 6

seconds. It should be understood, however, that the parameters of the through-air bonder depend on factors such as the type of polymers used and thickness of the web.

Lastly, the finished web is wound onto the winding roller 42 and is ready for further treatment or use. When used to make liquid absorbent articles, the fabric of the present invention may be treated with conventional surface treatments or contain conventional polymer additives to enhance the wettability of the fabric.

For example, the fabric of the present invention may be treated with polyalkylene-oxide modified siloxanes and silanes such as polyalkylene-oxide modified polydimethyl-siloxane as disclosed in U.S. Pat. No. 5,057,361. Such a surface treatment enhances the wettability of the fabric.

When through-air bonded, the fabric of the present invention characteristically has a relatively high loft. The helical crimp of the filaments creates an open web structure with substantial void portions between filaments and the filaments are bonded at points of contact. The through-air bonded web of the present invention typically has a density of from about 0.015 g/cc to about 0.040 g/cc and a basis weight of from about 0.25 to about 5 oz. per square yard and more preferably from about 1.0 to about 3.5 oz. per square yard.

Filament linear density generally ranges from less than 1.0 to about 8 denier. As discussed above, the crimp enhancement additive of the present invention allows for the production of highly crimped, fine filaments. In the past, naturally crimped fine filaments were difficult if not impossible to produce. According to the present invention, filaments having a natural crimp

of at least about 10 crimps per inch can be produced at linear densities less than 2 denier, and particularly at less than about 1.2 denier. For most nonwoven webs, it is preferable for the filaments to have from about 10 crimps per inch to about 25 crimps per inch. Of particular advantage, filaments having a natural crimp in the above range can be produced according to the present invention at a lower linear density than what has been possible in the past.

Thermal point bonding may be conducted in accordance with U.S. Pat. No. 3,855,046, the disclosure of which is incorporated herein by reference. When thermal point bonded, the fabric of the present invention exhibits a more cloth-like appearance and, for example, is useful as an outer cover for personal care articles or as a garment material.

Although the methods of bonding shown in **FIG. 1** are thermal point bonding and through-air bonding, it should be understood that the fabric of the present invention may be bonded by other means such as oven bonding, ultrasonic bonding, hydroentangling or combinations thereof. Such bonding techniques are well-known to those of ordinary skill in the art and are not discussed here in detail.

Although, the preferred method of carrying out the present invention includes contacting the multicomponent filaments with aspirating air, the present invention encompasses other methods of activating the latent helical crimp of the continuous filaments before the filaments are formed into a web. For example, the multicomponent filaments may be contacted with air after quenching but upstream of the aspirator. In addition, the multicomponent filaments may be contacted with air

between the aspirator and the web forming surface.

Furthermore, the filaments may also be exposed to electromagnetic energy such as microwaves or infrared radiation.

Once produced, the nonwoven webs of the present invention can be used in many different and various applications. For instance, the webs can be used in filter products, in liquid absorbent products, in personal care articles, in garments, and in various other products.

The present invention may be better understood with reference to the following Examples.

Example No. 1

The following Example was conducted in order to compare the differences between filaments and nonwoven webs made with the crimp enhancement additive of the present invention and filaments and nonwoven webs constructed without the crimp enhancement additive.

Two bicomponent spunbond fabrics were produced generally in accordance with the process disclosed in US Patent 5,382,400 (Pike, et al). In both fabrics, the filaments were round in cross section with the two components arranged in a side-by-side configuration. One side of the filaments was made primarily of polypropylene (Exxon 34455), while the other side was made primarily of polyethylene (Dow 61800). In both fabrics, the polypropylene (PP) side contained in an amount of 2% by weight an additive composed of 50% polypropylene and 50% TiO_2 .

In the first fabric (Fabric A), in accordance with the present invention, the polyethylene (PE) side contained in an amount of 2% by weight a random copolymer of 14% butylene and 86% propylene (Union Carbide DS4D05). The polyethylene side of the other fabric (Fabric B), on the other hand, was 100% polyethylene.

Both fabrics were produced at a total polymer throughput of 0.35 ghm of polymer per hole at a hole density of 48 holes per inch of width and were through air bonded at an air temperature of 265° F.

Fabric A was produced at a line speed of 44 feet per minute, while Fabric B was produced at 37 feet per minute. Line speed was used to control basis weight, all other process conditions remained the same. Both fabrics had a basis weight of 2.6 ounces per square yard (osy).

The fabrics were tested for tensile peak load, peak strain and peak energy (3" strips) in both the machine direction (MD) and cross-machine direction (CD) according to ASTM D-5035-90 and for caliper under a load of 0.05 psi with a Starrett-type caliper tester. Fabric density was calculated from basis weight and caliper. Fiber crimp was rated on a subjective 1 to 5 scale with 1 = no crimp and 5 = very high crimp. Fiber linear density was calculated from the diameter of the filaments (measured by microscope) and the density of the polymer. The strength of the unbonded web was determined by collecting a length of fabric that had not yet entered the bonder and gently laying it on the floor. The fabric was then slowly and gently lifted by one end until tensile failure was noted. The length of the fabric that was lifted at the point of tensile failure was recorded as the breaking length of the unbonded web.

The test results are shown on the following table.

Properties of Fabrics A & B

	<u>Fabric A</u>	<u>Fabric B</u>
Filament Linear Density (denier)	1.3	1.3
Filament Crimp Index	4.0	1.0
Fabric Basis Weight (osy)	2.6	2.6
Fabric Caliper (in)	0.135	0.090

Fabric Density (g/cc)	0.026	0.038
Unbonded Fabric Tensile		
Breaking Length (in)	66	18
Bonded Fabric Tensile Properties:		
MD Peak Load (lb)	6.5	10.9
MD Peak Strain (%)	46	20
MD Peak Energy (in-lb)	4.7	4.4
CD Peak Load (lb)	10.6	22.3
CD Peak Strain (%)	138	66
CD Peak Energy (in-lb)	24	32

The results show that Fabric A, relative to Fabric B, is composed of filaments having greater crimp and has a greater caliper (and therefore, lower density). Fabric A further has much greater unbonded web strength. While the tensile peak loads of Fabric B are about twice as large as those of Fabric A, the peak strain values of Fabric A are greater than those of Fabric B by about the same factor. Fabric peak energies, particularly in the machine direction, are similar.

Of particular significance, it is noted that the linear densities of both sets of filaments were very low, at about 1.3 denier. As shown, the filaments made containing the crimp enhancement additive of the present invention had a high natural crimp while the filaments not containing the additive experienced no significant crimp. As described above, in the past, it was very difficult to create a naturally crimped filament at low linear densities.

Example No. 2

The following example was conducted in order to demonstrate the ability of the additive of the present invention to facilitate mixing between different polymeric materials.

Polyethylene/polypropylene bicomponent filaments were produced and formed into a spunbond nonwoven web generally in accordance with the process described in Example 1 and disclosed in U.S. Patent No. 5,382,400 to Pike, et al.. The polyethylene side of the bicomponent filaments contained 20% by weight reclaim polymer. Specifically, the reclaim polymer was a mixture of polypropylene and polyethylene that had been collected from the trimmings of a previously formed nonwoven web.

In accordance with the present invention, the polyethylene component also contained 5% by weight of the butylene/propylene random copolymer identified in Example 1.

It was observed that by adding the butylene/propylene copolymer of the present invention, the reclaim polymer readily blended with the polyethylene component and produced a polymeric material that could be spun into filaments, which, in turn, could be naturally crimped. Further, it was discovered that filaments with very low linear densities could be produced. For instance, at a polymer throughput of 0.4 ghm and at a fiber draw pressure of 7.4 psi, filaments were produced having a linear density of 1.18 denier.

In the past, attempts have been made to produce bicomponent filaments containing reclaim polymer. Absent adding the additive of the present invention, however, it was not possible to spin the polymer mixture into filaments.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be

understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038 1039 1040 1041 1042 1043 1044 1045 1046 1047 1048 1049 1050 1051 1052 1053 1054 1055 1056 1057 1058 1059 1060 1061 1062 1063 1064 1065 1066 1067 1068 1069 1070 1071 1072 1073 1074 1075 1076 1077 1078 1079 1080 1081 1082 1083 1084 1085 1086 1087 1088 1089 1090 1091 1092 1093 1094 1095 1096 1097 1098 1099 1100 1101 1102 1103 1104 1105 1106 1107 1108 1109 1110 1111 1112 1113 1114 1115 1116 1117 1118 1119 1120 1121 1122 1123 1124 1125 1126 1127 1128 1129 1130 1131 1132 1133 1134 1135 1136 1137 1138 1139 1140 1141 1142 1143 1144 1145 1146 1147 1148 1149 1150 1151 1152 1153 1154 1155 1156 1157 1158 1159 1160 1161 1162 1163 1164 1165 1166 1167 1168 1169 1170 1171 1172 1173 1174 1175 1176 1177 1178 1179 1180 1181 1182 1183 1184 1185 1186 1187 1188 1189 1190 1191 1192 1193 1194 1195 1196 1197 1198 1199 1200 1201 1202 1203 1204 1205 1206 1207 1208 1209 1210 1211 1212 1213 1214 1215 1216 1217 1218 1219 1220 1221 1222 1223 1224 1225 1226 1227 1228 1229 1230 1231 1232 1233 1234 1235 1236 1237 1238 1239 1240 1241 1242 1243 1244 1245 1246 1247 1248 1249 1250 1251 1252 1253 1254 1255 1256 1257 1258 1259 1260 1261 1262 1263 1264 1265 1266 1267 1268 1269 1270 1271 1272 1273 1274 1275 1276 1277 1278 1279 1280 1281 1282 1283 1284 1285 1286 1287 1288 1289 1290 1291 1292 1293 1294 1295 1296 1297 1298 1299 1300 1301 1302 1303 1304 1305 1306 1307 1308 1309 1310 1311 1312 1313 1314 1315 1316 1317 1318 1319 1320 1321 1322 1323 1324 1325 1326 1327 1328 1329 1330 1331 1332 1333 1334 1335 1336 1337 1338 1339 1340 1341 1342 1343 1344 1345 1346 1347 1348 1349 1350 1351 1352 1353 1354 1355 1356 1357 1358 1359 1360 1361 1362 1363 1364 1365 1366 1367 1368 1369 1370 1371 1372 1373 1374 1375 1376 1377 1378 1379 1380 1381 1382 1383 1384 1385 1386 1387 1388 1389 1390 1391 1392 1393 1394 1395 1396 1397 1398 1399 1400 1401 1402 1403 1404 1405 1406 1407 1408 1409 1410 1411 1412 1413 1414 1415 1416 1417 1418 1419 1420 1421 1422 1423 1424 1425 1426 1427 1428 1429 1430 1431 1432 1433 1434 1435 1436 1437 1438 1439 1440 1441 1442 1443 1444 1445 1446 1447 1448 1449 1450 1451 1452 1453 1454 1455 1456 1457 1458 1459 1460 1461 1462 1463 1464 1465 1466 1467 1468 1469 1470 1471 1472 1473 1474 1475 1476 1477 1478 1479 1480 1481 1482 1483 1484 1485 1486 1487 1488 1489 1490 1491 1492 1493 1494 1495 1496 1497 1498 1499 1500 1501 1502 1503 1504 1505 1506 1507 1508 1509 1510 1511 1512 1513 1514 1515 1516 1517 1518 1519 1520 1521 1522 1523 1524 1525 1526 1527 1528 1529 1530 1531 1532 1533 1534 1535 1536 1537 1538 1539 1540 1541 1542 1543 1544 1545 1546 1547 1548 1549 1550 1551 1552 1553 1554 1555 1556 1557 1558 1559 1560 1561 1562 1563 1564 1565 1566 1567 1568 1569 1570 1571 1572 1573 1574 1575 1576 1577 1578 1579 1580 1581 1582 1583 1584 1585 1586 1587 1588 1589 1590 1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603 1604 1605 1606 1607 1608 1609 1610 1611 1612 1613 1614 1615 1616 1617 1618 1619 1620 1621 1622 1623 1624 1625 1626 1627 1628 1629 1630 1631 1632 1633 1634 1635 1636 1637 1638 1639 1640 1641 1642 1643 1644 1645 1646 1647 1648 1649 1650 1651 1652 1653 1654 1655 1656 1657 1658 1659 1660 1661 1662 1663 1664 1665 1666 1667 1668 1669 1670 1671 1672 1673 1674 1675 1676 1677 1678 1679 1680 1681 1682 1683 1684 1685 1686 1687 1688 1689 1690 1691 1692 1693 1694 1695 1696 1697 1698 1699 1700 1701 1702 1703 1704 1705 1706 1707 1708 1709 1710 1711 1712 1713 1714 1715 1716 1717 1718 1719 1720 1721 1722 1723 1724 1725 1726 1727 1728 1729 1730 1731 1732 1733 1734 1735 1736 1737 1738 1739 1740 1741 1742 1743 1744 1745 1746 1747 1748 1749 1750 1751 1752 1753 1754 1755 1756 1757 1758 1759 1760 1761 1762 1763 1764 1765 1766 1767 1768 1769 1770 1771 1772 1773 1774 1775 1776 1777 1778 1779 1780 1781 1782 1783 1784 1785 1786 1787 1788 1789 1790 1791 1792 1793 1794 1795 1796 1797 1798 1799 1800 1801 1802 1803 1804 1805 1806 1807 1808 1809 1810 1811 1812 1813 1814 1815 1816 1817 1818 1819 1820 1821 1822 1823 1824 1825 1826 1827 1828 1829 1830 1831 1832 1833 1834 1835 1836 1837 1838 1839 1840 1841 1842 1843 1844 1845 1846 1847 1848 1849 1850 1851 1852 1853 1854 1855 1856 1857 1858 1859 1860 1861 1862 1863 1864 1865 1866 1867 1868 1869 1870 1871 1872 1873 1874 1875 1876 1877 1878 1879 1880 1881 1882 1883 1884 1885 1886 1887 1888 1889 1890 1891 1892 1893 1894 1895 1896 1897 1898 1899 1900 1901 1902 1903 1904 1905 1906 1907 1908 1909 1910 1911 1912 1913 1914 1915 1916 1917 1918 1919 1920 1921 1922 1923 1924 1925 1926 1927 1928 1929 1930 1931 1932 1933 1934 1935 1936 1937 1938 1939 1940 1941 1942 1943 1944 1945 1946 1947 1948 1949 1950 1951 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 272